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## PROCESS FOR THE PHOTOTHERMOGRAPHIC PRODUCTION OF IMAGES

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The subject of the invention is the industrial exploitation of an observation that has become known to some extent over the last few years by the term "photothermal reaction," concerning the behavior of a group of light-sensitive substances. These substances, e.g., silver acetylide, have the property of

decomposing spontaneously at a certain temperature. On the other hand, the substances can be ignited even at room temperature if they are struck by light of adequate energy. However, the energy expenditure that is required for ignition falls in proportion to the extent to which the substances have been brought to a higher temperature level and finally converges to the value of zero for the required light energy on reaching the dark reaction temperature that amounts to 225°C in the case of silver acetylide, for example.

One can also characterize the typical behavior of such photothermal reactors by combining the light intensity  $i$  and the exposure time  $t$  to give the product  $it$ , whereby this product is a constant at each temperature. The quantity  $it$  falls with increasing temperature and finally reaches the value of zero at the (dark) ignition temperature.

It has now been found that one can considerably widen the use of photothermal reactions and utilize them for the preparation of photographic pictures, reproductions, and visible recordings of the most widely differing types if one subjects a photothermally reacting layer to the additional action of an energy field during exposure, whereby the photothermally active component of this layer is brought to an elevated thermal energy level as a result of the absorption of field energy that can be taken, for example, from a capacitative high frequency field in order to attain the situation where a large proportion of the molecules of the active component pass into a state of thermal excitation in which the physical or chemical reaction that is necessary for the formation of an image can be triggered with the smallest possible quantity of expended light energy.

In this connection, it has been found that it is necessary to considerably enlarge the concept of photothermal reactions. If, for example, one subjects a normal photographic layer, e.g., a silver bromide emulsion, to certain experimental conditions, then it exhibits the typical characteristics of a photothermal reaction. In this regard, it is necessary, briefly, to bring the silver halide of this emulsion to an elevated temperature comprising only the duration of the exposure. The normal means for heating the photographic emulsion are not usable here since, in this way, the layer-forming agents, gelatin or albumin, would be destroyed. Selective heating of the emulsion that exclusively affects the silver bromide particles and that is capable of exact control on a time basis can, however, be carried out if one subjects it to the action of a capacitative high frequency field. This selective heating arises because the silver halides have a significantly elevated dielectric loss angle relative to the colloid in the layer and relative to the support. As a result of this, it is possible, on terminating the exposure, to produce darkening that is controllable at will on a photographic layer after development only by means of the action of the high frequency, whereby the photographic layer and the support are not damaged. Since photothermal layers other than those that are supported on silver halides are also subsequently described, in which physical reactions are exploited for the preparation of copies; these will be described together under the general concept of "photothermographic layers" in the following sections, with the inclusion of previously known photographic layers.

According to the invention, any desired photographic emulsion is subjected to the action of a capacitative high

frequency field during exposure for the purpose of increasing its sensitivity to light. In order to achieve a maximum increase in light sensitivity, the following requirements have to be observed in this regard.

1. The action of the high frequency field and the exposure must take place simultaneously.

2. The duration of the action of the high frequency field may neither be less than nor greater than the duration of the exposure.

3. The product of the field intensity and the duration of the action of the high frequency field may not exceed the maximum value for incipient fogging in the dark.

4. The exposure duration must be selected so that it is as short as possible.

In order to achieve homogeneous action of the high frequency field over the entire surface of the photothermographic layer that is being subjected to exposure, the following arrangements of the high frequency electrodes in the photothermographic camera are used according to the invention.

The material that is to be exposed, for example, a photographic film, is located between two flat electrodes that correspond, in terms of the size of their surface, to the surface area of the exposed image. In this regard, the electrode that is turned in the direction of the width of the exposure is constructed in the form of a grid consisting of small parallel rods or wires. In this connection, the partial covering over of the image that is to be exposed by the grid can be avoided in terms of its effects if, during the exposure, the electrode is displaced parallel to the plane of the layer and vertically to

the rod direction of the grid lattice by one or more grid widths. In the case of camera arrangements that are set up with a slit diaphragm, the slit diaphragm that moves closely over the plane of the layer can be constructed in such a way that it is a component of a high frequency field that is formed by two electrodes, whereby the electrodes simultaneously delineate the optical width of the part of the image that is incident through the slit. As a consequence of the scatter effect of this high frequency field, a portion of the lines of force that are located in the slit zone penetrate the photothermographic layer so that, as a result of this, simultaneity of exposure and high frequency action is automatically ensured. A modification of this arrangement can be achieved for the purpose of more effective penetration of the photothermographic layer by high frequency radiation, using only the slit diaphragm as an electrode for the high frequency field, whereas the second electrode, is always located at the same height relative to the aperture of the slit diaphragm, is active from the back of the photographic film or plate.

According to the invention, the use of photothermal reactions is limited not only to increasing the sensitivity of previously known photographic emulsions but also comprises novel photothermographic layers that will be described in the following sections. Thus, for the preparation of such layers that are capable of copying, so-called fusion pigments can also be used that possess the property of changing over from the solid to a liquid state of average viscosity at a particular temperature that is not excessively high, within a narrowly delineated range of temperatures. Such substances can be obtained, for example,

by melting a fusible carrier with a colored pigment and, after solidification, grinding this mixture to a particle size that is as fine as possible. In this connection, the following technological requirements are set for the fusible carrier:

1. a narrow fusion range
2. a low vapor pressure (boiling point  $>300^{\circ}\text{C}$ )
3. chemical and physiological inertness
4. a low refractive index
5. low solubility in water
6. low values for the specific heat and the heat of fusion
7. the capability of forming supercooled melts
8. low inherent color
9. low manufacturing cost
10. a dielectric loss angle that is as high as possible
11. brittle consistency

A selection of substances that meet these requirements to some extent and whose fusion temperatures lie in the range from  $48$  to  $136^{\circ}\text{C}$ , that is technologically favorable for the present purpose, is listed below:

1. benzalacetophenone
2. benzil
3. benzoin
4. benzophenone
5. 2-chloroacetanilide
6. 3-chloroacetanilide
7. dibenzalacetone
8. dibenzoylmethane
9. dioxybenzophenone
10. diphenyl-2-carboxylic acid

11. diphenylphthalide
12. diphenylsulfone
13. glutaric acid
14. hexaethylbenzene
15. carbonic acid diphenyl ester
16. montanic acid
17. 4-nitrodiphenyl
18. 6-nitro-o-cresol
19. tetrahydronaphthol (5,6,7,8)
20. tribenzoin
21. triphenylamine
22. cinnamic acid anhydride

In this connection, it is expedient to use fusible carriers that comprise mixtures of these substances, whereby eutectic mixtures are especially suitable. As an example of a eutectic mixture that is suitable for this purpose, a benzil-benzoin mixture, with 18% benzoin and a melting point of 84°C, has proven to be valuable in practice.

In regard to the colored pigment, the following properties are desired in addition to requirements 2, 3, 5, 9 and 10 that were mentioned for the pigment carrier:

1. high covering power
2. a high refractive index
3. the capability of forming a colloidal dispersion with the fusible carrier.

Mention may be made of carbon black as an example of a substance that fulfills these requirements superbly.

For the preparation of a photothermographic layer that is constructed on the basis of fusion pigments, it is also necessary

that the fusion pigment particles be contained in the layer that consists of a binding agent, in the form of a dispersion. In addition to requirements 2, 3, 4, 5, 6, 8 and 9 that have already been set for the fusible carriers, additional requirements are also set for this layer binding agent that, in addition to a low dielectric loss angle, should possess good adhesion to the support and extensive inertness with respect to the fusion pigment. In addition, the thermoplastic properties of the binding agent must satisfy certain conditions that are not simple to define, however, since these have to be adapted to the physical properties of the fusion pigment that is used in each case. Such layer binding agents can be prepared, for example, from paraffins and synthetic waxes, whereby, in terms of their drop point temperature, these should expediently lie somewhat below the fusion temperature of the fusion pigment that is used in each case. In addition, highly viscous substances such as, for example, polyvinyl ether, possibly with an addition of highly polymeric styrene, have proven their suitability as binding agents. The demand for light by these photothermographic layers is least when the quantity of fusion pigment that is dispersed in them is as low as possible, whereby the technologically necessary minimum expenditure of the quantity of the substance depends on the fineness to which one is successful in completely grinding the fusion dye. In addition, the quantity of binding agent and thus the layer thickness of the fusion pigment dispersion are of considerable influence on image contrast.

Such a photothermographic layer that has been applied, for example, to a transparent sheet of low dielectric loss angle results in a "copying sheet" with which a copying process can be

carried out as follows: if this copying sheet is adequately exposed from the back, together with the simultaneous action of a HF field, then the pigment particles that are contained in the layer are brought to the point of fusion as a result of this, whereby the number of particles that have completely melted per unit surface area is proportional to the light energy that has been expended. The molten portion of the pigment particles is transferred to an image receiving layer that consists, e.g., of paper, either during the exposure or shortly thereafter, by means of a compressing device, whereby the image receiving layer lies on the layer side of the sheet. Especially rational implementation of image transfer results from the following arrangement, for example: the copying sheet is constructed in the form of a belt and is drawn past a slit diaphragm together with the negative belt that is placed thereon and the image receiving paper that is placed underneath. The luminescent filament material of a projection lamp is fashioned, by means of projection optics, into a luminescent belt in this diaphragm, whereby the belt runs transversely to the negative belt. The longitudinal boundaries of the slit diaphragm form two HF electrodes so that a HF field is formed in this slit of the diaphragm that penetrates, to some extent, the belts that move past under the slit. Using a compressing device constructed as a single unit with the HF electrodes, the belts are pressed together immediately after exposure for the purpose of pigment transfer to the image receiving paper. Whereas, in the case of the present arrangement of electrodes, only the scattered HF field is utilized for penetrating radiation of the copying material, more effective penetrating radiation of the copying

material can be achieved by arranging one electrode, in each case, in front of and behind the copying material. For example, the electrode arrangement can be made in such a way that the slit diaphragm is constructed in the form of one electrode, whereas the second electrode is arranged opposite the diaphragm aperture on the unexposed rear of the copying material and is held in such a way in terms of its dimensions that a maximum of field lines penetrates the copying material in the zone of the slit opening.

For the preparation of photothermographic layers, use can also be made of substances that possess the property of being transformed, during exposure, from the soluble to the insoluble state within a narrow temperature range in the way in which they are characterized best of all, for example, by the known behavior of albumin and starch. Thus the denaturing of egg albumin starts at 69°C with a very large temperature coefficient and achieves a 90-fold higher rate of reaction even at 76°C. Conversely, as is known, potato starch is virtually insoluble up to a temperature of 55°C and then, in an instant, forms a glue at a temperature of 63°C. Polyvinyl ether behaves similarly, whereby it is insoluble in water at a temperature of 32°C but differs from the aforementioned substances by way of the feature that the process is reversible. Mention may be made, for example, of the following as being especially suitable substances for this purpose.

1. Polyvinyl alcohol that becomes insoluble in water at a temperature of 100°C.

2. Dimethylol urea that results in a solid water-insoluble condensation product at 137°C.

These substances, mixed with carbon black for coloration purposes and in order to increase their dielectric loss angle, result in photothermographic layers that are transformed from the water-insoluble hydrophobic state within a narrow temperature range. Recordings on copying sheets that have been provided with such a layer can be transferred in a similar manner to other surfaces such as copying sheets according to the fusion pigment process.

The advantage of this process is a lower requirement for light relative to the fusion pigment process; in this connection, however, a negative would again arise from a negative as the source image and this would be undesired with the practice of copying that is customary today. According to the invention, the proposal is therefore made of reusing the remaining image content of the copying sheet as a positive image in such a way that, after transferring the soluble parts of the image, this sheet is provided with a background that makes the residual content of the image visible. For this purpose, use can be made, for example, of a weldable thermoplastic material as, for example, the support for the copying sheet, whereby the thermoplastic material is welded to a paper underlayer after copying. An advantage of this method would be that such copies would correspond to the currently used makeup of photographic paper images without the disadvantage of having to accept the slight distortion of previous photographs. A further advantage of this method would be that, during the welding of the sheet, the desired surface configuration of the image could be implemented simultaneously in each case. In order to utilize these advantages during the preparation of images according to the fusion pigment process,

the proposal is made, according to the invention, to use the same method of reusing the image that remains on the copying sheet and, in this way, to start out from a positive transparency as the source image. In order to increase the profitability of this method, the proposal is also made to use a continuous belt as the copying surface for detaching the transferable pigment fraction of the copying sheet, whereby the continuous belt runs through a cleaning device for removing the pigment fractions that are taken up by it during copying.

In order to produce multicolor or, especially, naturally colored copies that are prepared using a colored source image, the proposal is also made to prepare photothermographic layers whose photothermally active component consists of a mixture of particles in several different colors, i.e., consisting, for example, of a mixture of particles in four different color tones in the type of composition in which they are used for the generation of four color prints. In this connection, these pigment particles are brought into action by absorption and, in terms of their pigment composition, they correspond, in each case, to the complementary value of the colored components of the incident light.

### Claims

1. Process for photothermographic image production, characterized in that photothermographically sensitive layers are simultaneously subjected to an exposure and to the equally long action of an energy field and, after exposure, the photothermally modified or unmodified parts are removed from the layers whereby,

in the case of the formation of an initially invisible image, this is also transformed into a visible image.

2. Process according to Claim 1, characterized in that photothermally reacting layers are used that contain a component that, as a consequence of increased energy absorption (engendered, for example, by the atomic weight, the light absorption value or the dielectric loss angle) experiences selective heating relative to the other layer components and the support.

3. Process for the production of a photothermographic image according to Claim 1, characterized in that, for this purpose, use is made of layers that contain silver halide.

4. Process for the production of a photothermographic image according to Claim 1, characterized in that, for this purpose, use is made of layers that contain pigment particles that become fusible or insoluble at an elevated temperature.

5. Process according to Claims 1-4, characterized in that two flat electrodes act from different sides on the photothermally reacting layer, of which the electrode that is turned toward the exposure side is constructed in the form of a grid with rods and, during the time of the exposure, it is displaced by one or more grid rod widths parallel to the plane of the layer and vertically to the direction of the rod.

6. Process according to Claims 1-4, characterized in that, in order to produce a HF field that acts homogeneously on a photothermally reacting layer of any desired size, one guides the two electrodes in their relative movement parallel to the plane of the layer during the time of the exposure, whereby these are also components of a slit diaphragm through which the exposure

takes place and that, as a result of this, the exposed image plane is scanned line by line.

7. Process according to Claim 5, characterized in that the high frequency irradiation process is carried out with an electrode that is constructed in the form of a slit diaphragm, whereas a second electrode acts on the copying material from the unexposed side opposite the diaphragm opening, whereby the second electrode is held in such a way in terms of its dimensions that a maximum of field lines penetrates the copying material in the zone of the slit opening.

8. Photothermally reacting layer for the implementation of the process according to Claims 1 and 2, characterized in that the photothermally active component of this layer comprises fusible pigment particles whose melting point lies above the temperature to which the layer is maximally exposed during normal usage.

9. Photothermally reacting layer according to Claims 1 and 2, characterized in that the photothermally active component of this layer possesses the property of changing from a soluble state to an insoluble state within a narrow temperature range.

10. Photothermally reacting layer according to Claims 1, 2, 8 and 9, characterized in that the photothermally active component of this layer consists of a mixture of particles in several different colors.

11. Process according to Claims 1-7, characterized in that a layer that is located on a transparent sheet is exposed from the back under the action of a HF field according to Claims 8 and 10 and, simultaneously, by means of a compressing device, the parts of the image that have become transferrable (as a result of

exposure and HF irradiation) are transferred from the photothermally reacting layer to an image receiving surface consisting, for example, of paper lying on the layer side of the sheet.

12. Process according to Claim 11, characterized in that the image remaining on the transparent copying sheet is provided with an underlayer that makes the contents of the image visible by reflection.